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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Foams from Vinyl Ether Prepolymers

We, CANADIAN INDUSTRIES LIMITED, a corporation of Canada, 630 Dorchester Boulevard West, Montreal, Province of Quebec, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to improved compositions suitable for the production of foamed cellular polymeric materials and to the improved foamed cellular polymeric materials obtained therefrom.

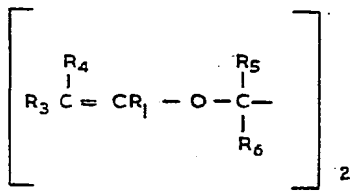
In United Kingdom Patent No. 991,970 there are described foamable compositions of a novel type which comprise at least one polymerisable vinyl ether containing at least two vinyl groups per molecule, a foaming agent, an acidic catalyst and, optionally at least one compound reactive with said vinyl ether such as a polyhydric phenol, an aliphatic polyhydric alcohol, an expoxidised material, a polycarboxylic acid, a polyamide or a polycarbamate. The compositions yield foamed cellular polymeric materials which are superior to the known polyurethanes from the standpoint of ingredient toxicity and are superior to the known polystyrene foams for convenience in foaming-in-place.

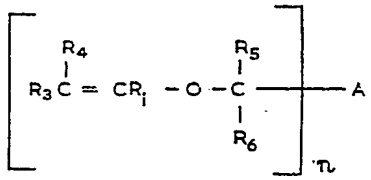
Despite their many useful properties, however, the aforesaid novel foams expand and set quickly, thus introducing difficulties in filling large spaces with uniform bodies of foam free of cracks. Many of the aforesaid novel foams also lack resilience, have friable skins, and when employed in low density form are dimensionally unstable.

It has now been found that if in the above type of foamable compositions, a polymerisable ether is first reacted with the ether-reactive ingredient to form a prepolymer, foams made from this prepolymer ingredient admixed with a foaming agent and an acidic catalyst, with or without additional polymerisable ether and/or polymerisable ether-reactive compounds possess a longer reaction time before setting, are more resilient, have good skins, better adhesion and are dimensionally stable even when in low density form.

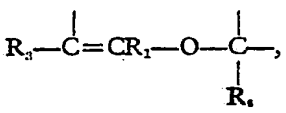
Thus according to the present invention there are provided foamable compositions comprising (1) at least one prepolymer which is the reaction product of at least one polymerisable ether of the general formula—

I $$R_3C=CR_1—O—R_1C=CR_2$$

II 

III 

wherein n is an integer of minimum value of 2, R_1, R_2 and R_4 are hydrogen or alkyl-radicals, R_3 is hydrogen, a halogen atom or a hydrocarbyl radical, R_4 and R_5 taken together are two hydrogen atoms, two alkyl radicals or an alkylene or substituted alkylene group forming a cyclic structure with the group



and A is a linking group having a valency equal to n, with a compound reactive with the unsaturated linkage of the said polymerisable ether selected from alcohols, polyhydric phenols, carboxylic acids, polycarbamates and polyamides, (2) a volatile foaming agent and (3) an acidic catalyst capable of polymerising a vinyl ether and optionally (4) at least one other ingredient selected from polymerisable ethers as hereinbefore defined, phenolic compounds, aliphatic alcohols, epoxidised materials containing at least one epoxide group per molecule, polycarboxylic acids, polyamides, polycarbamates and polymerisable α-β-ethylenically unsaturated compounds.

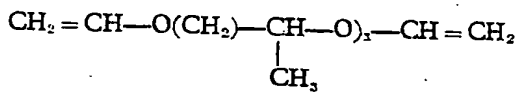
It has been found that suitable proportions of the ingredients for making the prepolymers of this invention are such as to provide at least one reactive group of the ether-reactive compound for each molecule of the polymerisable ether. The properties of the foamed products are dependant upon the equivalent weight of the prepolymer. For example when the ether-reactive compound is a polyhydric alcohol, rigid foams are obtained when the equivalent weight of the prepolymer is less than 270 per polymerisable ether group, semi-rigid foams requiring an oven cure result when the equivalent weight of the prepolymer lies between 270 and 350 per polymerisable ether group; and flexible foams foamable only in an oven at 60°C to 80°C result when the equivalent weight of the prepolymer is greater than 350 per polymerisable ether group. In the case of the said flexible foams the viscosity of the prepolymer is critical; if the viscosity is too low the foaming agent escapes prematurely, if the viscosity is too high inferior foams result. For flexible foams of this type a suitable viscosity range for the prepolymer is between 30 and 60 poises at room temperature.

The prepolymer may constitute from 35% to 98% by weight of the foamable compositions of the invention.

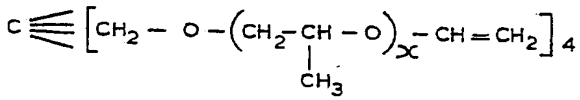
The foamable compositions of this invention may also include flame retardants, surfactants, dyes, fillers, stabilizers, antioxidants, plasticisers and viscosity modifiers.

The polymerisable ethers suitable for use in the foamable compositions of this invention, are as hereinbefore defined wherein two or more unsaturated groups are each joined to an ether oxygen atom.

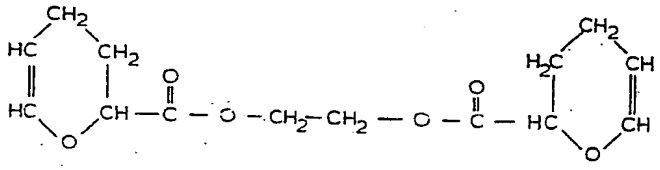
Examples of such polymerisable ethers are: divinyl ether, diisopropenyl ether, butanediol divinyl ether, ethers of alkylene oxide/polyol condensates of the formulae



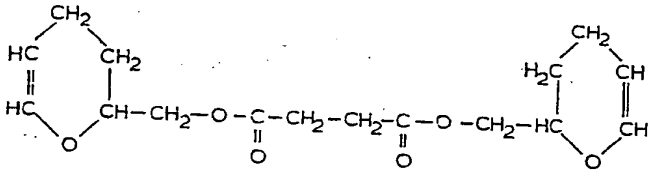
and



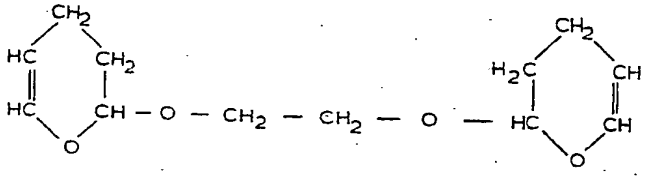
wherein x is any integer, 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro-2H - pyran - 2 - carboxylate) described hereinafter, 1,2 - ethanedioxy - bis(3',4'-dihydro - 2'H - pyran - 2' - carbonyl) of the formula



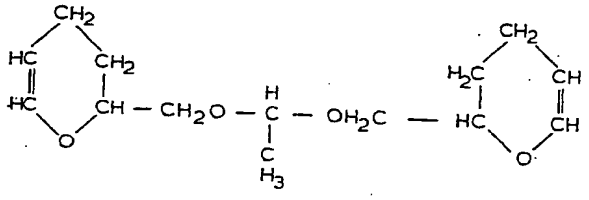
bis - (3,4 - dihydro - 2H - pyran - 2 - methyl) succinate of the formula



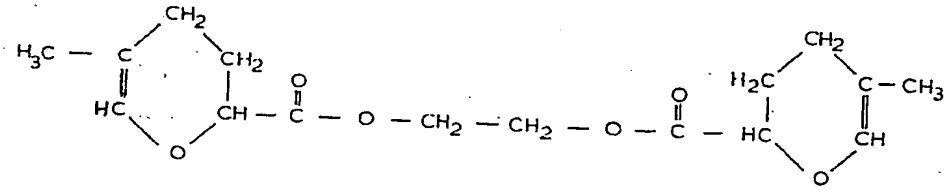
1,2 - bis(3',4' - dihydro - 2'H - pyran - 2' - oxy) ethane of the formula



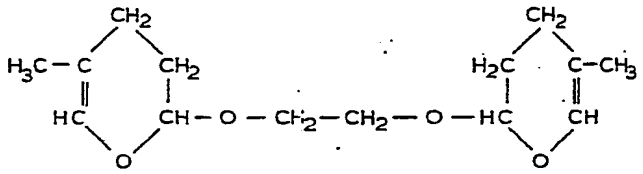
1,1 - bis(3',4' - dihydro - 2'H - pyran - 2' - methoxy) ethane of the formula



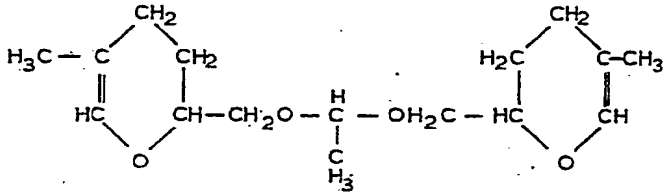
1,2 - ethanedioxy - bis(3',4' - dihydro - 5' - methyl - 2'H - pyran - 2' - carbonyl) of the formula



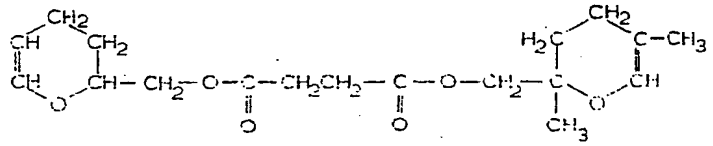
1,2 - bis(3'4' - dihydro - 5' - methyl - 2'H - pyran - 2' - oxy) ethane of the formula



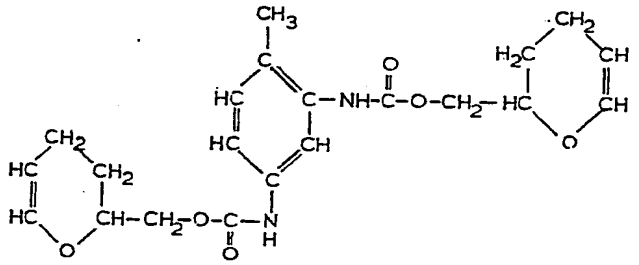
1,1 - bis(3',4' - dihydro - 5' - methyl - 2'H - pyran - 2' - methoxy) ethane of the formula



3,4 - dihydro - 2H - pyran - 2 - methyl (3,4 - dihydro - 5 - methyl - 2H - pyran-2,2-dimethyl) succinate of the formula



toluene - 2,4 - bis(3',4' - dihydro - 2'H - pyran - 2' - methyl) carbamate of the formula



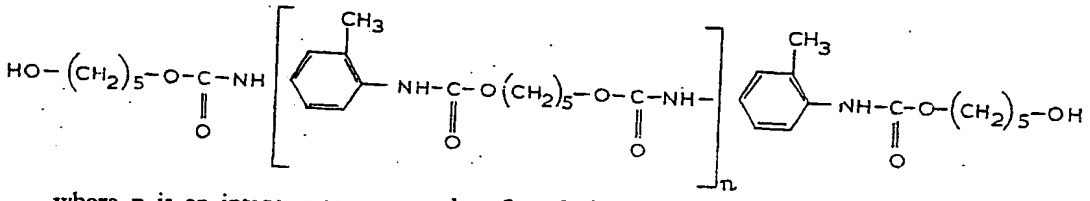
the tri-ester derived from three moles of 2-hydroxymethyl-3,4-dihydro-2H-pyran and one mole of orthophosphoric acid, and the esters derived from 2-hydroxymethyl-3,4-dihydro-2H-pyran and organic polybasic acids such as maleic and adipic acids. It has been found that the straight chain polymerisable ethers are more reactive than branched chain of cyclic polymerisable ethers. The ether groups in the molecule may be the same or different. It is desirable that the polymerisable ethers do not boil during the foam forming reaction.

The aliphatic monohydric or polyhydric alcohol ingredients of the prepolymers of the foamable compositions of this invention include amyl alcohol, 2-ethylhexyl alcohol, nonyl alcohol, n-decyl alcohol, ethylene glycol, propylene glycol, 1,3-butylene glycol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, glycerol, 1,2,6-hexanetriol, trimethylolethane, trimethylolpropane, castor oil, pentaerythritol, sugar alcohols, sugar alcohol-alkylene oxide condensates and hydroxyl containing esters and polyesters obtained by the condensation of polyhydric alcohols and polybasic acids.

The polyhydric phenol ingredients of the prepolymers include resorcinol, catechol, hydroquinone, 2:2-di-p-hydroxyphenyl propane, phloroglucinol, low molecular weight phenol terminated polycarbonates, the condensation products of phenols with aldehydes and ketones, etc.

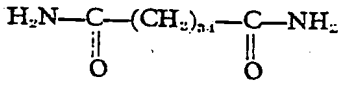
Suitable polycarboxylic acid ingredients of the prepolymers include succinic, glutaric, adipic, azelaic, maleic, fumaric, itaconic, phthalic, isophthalic, terephthalic, trimellitic, trimesic and chlorendic (1,4,5,6,7,7 - hexachlorobicyclo - [2,2,1] - 5-heptene - 2,3 - dicarboxylic acid) acids and polymerized unsaturated fatty acids such as the dimeric and trimeric acids, and free carboxylic group-containing esters and polyesters.

Suitable polycarbamate ingredients for the prepolymers include those derived from organic polyisocyanates and polyols such as the condensation product of tolylene diisocyanate and 1,5-pentanediol of formula



where n is an integer not greater than 3 and the low molecular weight condensation product of diphenylmethane 4,4'-diisocyanate and polypropylene glycol of molecular weight 425.

Among the suitable polyamides may be mentioned the diamide derived from dimerized linseed oil acids and having the formula



and the polyamide derived from isophthalic acid and pentamethylene diamine.

The prepolymer may be formed by simply mixing the ingredients. In some cases the reaction may be accelerated by heating. In most cases it is convenient to employ an acidic catalyst such as p-toluenesulphonic acid, hydrochloric acid or sulphuric acid.

Volatile foaming agents suitable for use in the foamable compositions of this invention are these which are soluble or dispersible in the other ingredients of the foamable compositions and are sufficiently volatile that they vaporize during the formation of the foamed polymeric materials. The heat of the catalyzed polymerisation reaction causes the foaming agent to boil and the vapour forms bubbles which expand during the polymerization reaction to give a low density foamed polymerized mass. Preferred foaming agents are the halogenated hydrocarbons such as trichloromonofluoromethane, dichlorotetrafluoroethane, trichlorotrifluoroethane, dibromodifluoromethane, dichlorohexafluorocyclobutane, methylene chloride, chloroform, trichloroethylene, carbon tetrachloride and perchloroethylene.

The acid catalysts suitable for promoting the foam-forming reaction include the strong proton-donating acids such as p-toluenesulphonic acid, and the Lewis acids such as boron trifluoride conveniently employed as the etherate. Compositions containing very reactive ethers such as butanediol divinyl ether can be catalyzed by p-toluenesulphonic acid but a Lewis acid catalyst is preferred for those compositions containing 3,4-dihydro-2H-pyranyl compounds including the 3,4-dihydro-2H-pyran-2-methy-(3,4-dihydro-2H-pyran-2-carboxylate) referred to hereinafter. It is possible to control the foam-forming reaction by employing catalyst combinations e.g. p-toluenesulphonic acid and boron trifluoride or boron trifluoride and trimethoxyboroxine. Other materials which are suitable as catalytic ingredients are ferric chloride, stannic chloride, phosphorus pentachloride, phosphoric acid, perchloric acid, trifluoroacetic acid, trichloroacetic acetic acid, fluoboric acid, boron trifluoride dihydrate, hydrogen fluoride, antimony pentafluoride, hexafluorophosphoric acid, lead fluoroborate, antimony fluoroborate, sulphuric acid and silicotungstic acid. The solvent in which the catalyst is dissolved also affects the catalyst reactivity, polypropylene glycol solutions of boron trifluoride etherate being less reactive than xylene solutions of said catalyst. Suitable proportions of catalyst are from 0.005% to 2.0% by weight of the compositions, but this range is not limiting since the amount of catalyst should be adjusted to the temperature of operation and the foam induction period required.

Catalysts used in the present invention are conveniently employed as 5% to 50% solutions in solvents, for example as solutions in monoethyl ether of ethylene glycol, the monoethyl ether of diethylene glycol, nitromethane, nitrobenzene, butyrolactone, acetone, n-butanol or diethyl ether.

Suitable flame retardants for incorporation in the foamable compositions include trichloroethylphosphate, 2:2 - bis - (3',5' - dibromo - 4' - hydroxyphenyl) propane, tris-(dibromopropyl) phosphate, chlorendic acid and polyvinyl chloride, with or without antimony oxide. The phenolic compound and the chlorendic acid serve both as flame-retardants and vinyl ether-reactive materials.

The preferred surfactants are those of the silicone type, examples of which are disclosed in U.K. Patents Nos. 923,403 and 930,635, i.e. being of the siloxane oxyalkylene copolymer type.

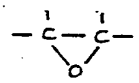
There may also be incorporated in the foaming compositions of the present invention one or more unreacted polymerisable ethers as hereinbefore defined or one or more compounds reactive with or copolymerisable with said polymerisable ethers.

Examples of suitable polymerisable ethers for incorporation in the compositions of the present invention are those polymerisable ethers mentioned hereinbefore.

Compounds reactive or copolymerisable with the said polymerisable ether which have been found especially useful for incorporation in the compositions of the present invention include phenolic compounds, aliphatic monohydric and polyhydric alcohols, expoxidised materials containing at least one epoxide group per molecule, acidic compounds containing at least two carboxylic acid groups per molecule, amido compounds containing at least two amido groups per molecule, carbamate compounds containing at least two carbamate groups per molecule and polymerisable alpha, beta-monoethylenically unsaturated compounds.

Examples of phenolic compounds, aliphatic monohydric and polyhydric alcohols, polycarboxylic acids, amido compounds containing at least two amido groups per molecule and carbamate compounds containing at least two carbamate groups per molecule which may be incorporated are as listed hereinbefore.

By "epoxidised materials containing at least one epoxide group per molecule" which may be incorporated are meant compounds containing at least one group of the formula



per molecule. Examples of such compounds are epichlorohydrin, styrene oxide, diallyl ether monoxide, cyclohexene oxide, glycidyl phenyl ether, glycidyl stearate, dipentene dioxide, vinyl cyclohexene dioxide, polyallyl glycidyl ether, diphenylolpropane diglycidyl ether, epoxidised polybutadiene, epoxidised styrene-butadiene copolymers and the resinous condensates of epichlorohydrin and aliphatic or aromatic polyols such as glycerol or 2,2-di-p-hydroxyphenyl propane.

Examples of polymerisable alpha, beta-monoethylenically unsaturated compounds are 3,4-dihydro-2H-pyran, 2-ethoxy-3,4-dihydro-2H-pyran, 2-alkyl-3,4-dihydro-2H-pyran, 2-phenyl-3,4-dihydro-2H-pyran, 1-decene, vinyl stearate, lauryl vinyl ether, dibutyl maleate, maleic anhydride, vinyl cyclohexene, alkyl acrylates, alkyl methacrylates and styrene.

Thus the foaming compositions of the present invention may contain in addition to the preformed reaction product, catalyst and foaming agent, a proportion of unreacted polymerisable ether and of a compound reactive therewith. The use of different proportions of such materials gives compositions which lead to the formation of foamed materials of widely differing properties. In order to obtain foamed materials of advantageous properties suitable for particular uses it is necessary to vary the proportions of preformed reaction product and other active ingredients according to their respective natures.

The preparation of the foams of this invention through the prior formation of a prepolymer results in foams that are superior to those formed directly from the foaming ingredients without the intermediate stage of prepolymer formation. The improved foams of this invention have greater resilience, better skins and, when being foamed, have a longer rise time. In addition it is possible using the methods of this invention to prepare foams that are dimensionally stable at reduced densities.

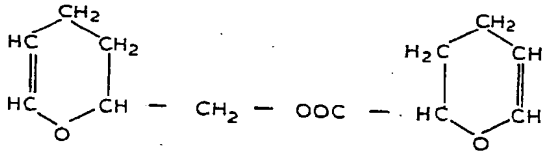
The ingredients of the foamable compositions may simply be mixed by stirring in a vessel and then quickly pouring into a mould. In some cases it is convenient to heat the composition in the mould to assist in the formation of the foam. The foaming ingredients may also be mixed in the space which is to be filled with foam if it is suitably shaped. When such stirred mixing is used, it is highly desirable that

a surfactant be added to the compositions in order to give foams of small cells. However, a surfactant is not always essential. For example, in certain foam-dispensing machines, the ingredients are mixed under pressure using a foaming agent which is gaseous at the mixing temperature, the pressure being controllably released, and the " frothed " mixture is then dispersed to the point of use. In such a " frothing " machine, a surfactant is not essential. However, in ordinary dispensing machines wherein the foaming compositions are dispensed before foaming starts, the use of a surfactant is often desirable. In many recipes, it has been found that reduction of the amount of surfactant to the point where the bubbles just burst as polymerization is complete gives foams of an " open cell " structure.

The foams of the invention in the flexible form may be used for upholstery, mattresses etc. In the rigid form they are eminently suited for heat insulating and sound absorbing purposes, either in closed cavities or as enveloping blankets.

The invention is illustrated but not limited by the following Examples.

A preferred polymerisable ether used in the Examples is 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate) of the following formula:



It may be prepared by the self-condensation of acrolein dimer (2-formyl-3,4-dihydro-2H-pyran) in the presence of about 0.3% of aluminium isopropoxide, the reaction temperature being held at 45°C. for 6 hours. A purified product may be obtained by flash distillation in a falling film still at 150°C. under vacuum, but satisfactory foams can be obtained with the undistilled product.

Example 1.

A prepolymer was prepared as follows: to 448 grams of 3,4-dihydro-2H-pyran-2-methyl(3,4-dihydro-2H-pyran-2-carboxylate) contained in a three necked flask fitted with stirrer, thermometer, funnel and nitrogen gas inlet were added 62 grams of ethylene glycol containing 0.06 gram p-toluenesulphonic acid. The mixture was heated under a blanket of nitrogen gas to 60°C. with stirring. When the exothermic reaction began, the temperature of the mixture was kept around 80°C. by cooling. When the temperature began to drop the cooling bath was removed and the reaction mixture was stirred for another hour. The infra-red absorption spectrum of the reaction product showed no absorption peak in the hydroxyl region.

The following mixture was prepared:

Prepolymer above	300 grams
Siloxane oxyalkylene copolymer type silicone surfactant	1.0 gram
Trichloromonofluoromethane	35 millilitres
3% boron trifluoride etherate in methylene chloride	22 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. After an induction period of 48 seconds the mixture foamed with a rise time of 72 seconds to give a rigid resilient foam with excellent texture and skin.

Example 2.

A prepolymer was prepared using the procedure of Example 1 employing as ingredients 672 grams of 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro-2H - pyran - 2 - carboxylate) and 159 grams of diethylene glycol containing 0.1 gram of p-toluenesulphonic acid.

The following mixture was prepared:

Prepolymer above	300 grams
Siloxane oxyalkylene copolymer type silicone surfactant	1.0 gram
Trichloromonofluoromethane	50 millilitres
20% boron trifluoride etherate in polypropylene glycol of molecular weight 425	5 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. After an induction period of 72 seconds, the mixture foamed with a rise period of 72 seconds to give a rigid, resilient foam which was non-brittle and non-friable.

EXAMPLE 3.

A prepolymer was prepared using the procedure of Example 1 employing as ingredients 672 grams of 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro-2H - pyran - 2 - carboxylate) and 156 grams of 1,5 - pentanediol containing 0.1 gram of p-toluenesulphonic acid.

The following mixture was prepared:

Prepolymer above	250 grams
Siloxane oxyalkylene copolymer type silicone surfactant	1.0 gram
Trichloromonofluoromethane	45 millilitres
20% boron trifluoride etherate in polypropylene glycol of molecular weight 425	4 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. After an induction period of 66 seconds, the mixture foamed with a rise period of 72 seconds to give a rigid resilient foam with good texture and skin.

EXAMPLE 4.

A prepolymer was prepared using the procedure of Example 1 employing as ingredients 896 grams of 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro-2H - pyran - 2 -carboxylate) and 228 grams of 2:2 - di - p - hydroxyphenyl propane containing 0.12 gram of p-toluenesulphonic acid.

The following mixture was prepared:

Prepolymer above	250 grams
Siloxane oxyalkylene copolymer type silicone surfactant	1.0 gram
Trichloromonofluoromethane	40 millilitres
20% boron trifluoride etherate in polypropylene glycol of molecular weight 425	4 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. After an induction period of 18 seconds, the mixture foamed with a rise time of 24 seconds. The rigid foam so produced showed improvement in resilience and skin over foams produced from the same vinyl ether and phenol ingredients but produced via the one stage process.

EXAMPLE 5.

A prepolymer was prepared using the procedure of Example 1 employing as ingredients 900 grams of 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro-2H - pyran - 2 -carboxylate) and 880 grams of polypropylene glycol of molecular weight 425 and hydroxyl number 255.0 (Niax Dioi PPG 425) (the word NIAX is a Registered Trade Mark) containing 0.5 gram of p-toluenesulphonic acid.

The following mixture was prepared:

Prepolymer above	75 grams
Siloxane oxyalkylene copolymer type silicone surfactant	1.0 gram
Trichloromonofluoromethane	20 millilitres
20% boron trifluoride etherate in polypropylene glycol of molecular weight 425	2 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. The mould containing the mixture was placed in an oven at 60°C. After a period of 1 hour a good flexible foam was obtained.

EXAMPLE 6.

A prepolymer was prepared using the procedure of Example 1 employing as ingredients 341 grams of 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro-2H - pyran - 2 -carboxylate) and 500 grams of a polyglycol of molecular weight 1000 and hydroxyl number of 170.4 (Niax Triol LG—168) (NIAX is a Registered Trade Mark) containing 0.5 gram of p-toluenesulphonic acid.

The following mixture was prepared:

Prepolymer above	15 grams
Prepolymer of Example 5	60 „
Siloxane oxyalkylene copolymer type silicone surfactant	1.0 gram
Trichloromonofluoromethane	20 millilitres
20% boron trifluoride etherate in polypropylene glycol of molecular weight 425	2 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. The mould containing the mixture was placed in an oven at 60°C. After a period of 1 hour a good flexible foam was obtained.

EXAMPLE 7.

A prepolymer was prepared using the procedure of Example 1 using as ingredients 336 grams of 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro - 2H - pyran-2-carboxylate), 500 grams of castor oil and 0.35 gram of *p*-toluenesulphonic acid dissolved in 3 millilitres of ethyl acetate.

The following mixture was prepared:

Prepolymer above	15 grams
Prepolymer of Example 5	60 „
Siloxane oxyalkylene copolymer type silicone surfactant	1.0 gram
Trichloromonofluoromethane	20 millilitres
20% boron trifluoride etherate in polypropylene glycol of molecular weight 425	2 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. The mould containing the mixture was placed in an oven at 60°C. After a period of 1 hour a very good flexible foam was obtained.

EXAMPLE 8.

A prepolymer was prepared using the apparatus employed in Example 1. 66 grams of glutaric acid were heated with 224 grams of 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate) at 70—75°C. for 3 hours under nitrogen atmosphere. The acid dissolved completely in about 1 hour. The product had an acid number of 28.7.

The following mixture was prepared:

Prepolymer above	25 grams
Siloxane oxyalkylene copolymer type silicone surfactant	0.1 gram
Trichloromonofluoromethane	5 millilitres
10% boron trifluoride etherate in polypropylene glycol of molecular weight 425	0.25 „

The mixture was stirred for 18 seconds with a mechanical stirrer and poured into a mould. The mixture foamed after an induction period of 7 seconds to give a very resilient rigid foam.

EXAMPLE 9.

A prepolymer was prepared by heating 20 grams of 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate) at 100°C. and stirring in 6 grams of chlorendic acid (1,4,5,6,7,7 - hexachlorobicyclo - [2.2.1] - 5 - heptene - 2,3 - dicarboxylic acid). The solid slowly dissolved and the mixture increased in viscosity indicating reaction. After 30 minutes the solution was decanted from the small amount of undissolved solid. 21.5 grams of material were thus obtained.

The following mixture was prepared:

Prepolymer above	21.5 grams
Siloxane oxyalkylene copolymer type silicone surfactant	0.25 „
Trichloromonofluoromethane	2.0 „
10% boron trifluoride etherate in polypropylene glycol of molecular weight 2025	1.0 gram

The mixture was stirred for 5 seconds with a mechanical stirrer and poured into a mould. Foaming occurred within 10 seconds to give a good looking fine cell foam. The foam was " self-extinguishing " by ASTM 1692—59—T.

EXAMPLE 10.

A prepolymer was prepared as follows: 31.5 grams (0.25 mole) of anhydrous phloroglucinol were dissolved in 180 grams (0.825 mole) of 3,4-dihydro-2H-pyran-2-methyl - (3,4 - dihydro - 2H - pyran - 2 - carboxylate) with stirring and heating. The mixture was maintained at 60°C. during the dropwise addition of 0.12 millilitres of a 20% solution of *p*-toluenesulphonic acid in ethylene glycol. The reaction mixture thickened and was then diluted with 90 grams of 3,4-dihydro-2H-pyran-2-methyl-(3,4-dihydro-2H-pyran-2-carboxylate) to give a heavy flowing liquid.

The following two mixtures were prepared:

Mixture A

Prepolymer above	17.5 grams
3,4 - dihydro - 2H - pyran - 2 - methyl-(3,4 - dihydro - 2H - pyran - 2 - carboxylate)	7.5 „
Siloxane oxyalkylene copolymer type silicone surfactant	0.1 gram
Trichloromonofluoromethane	5 grams

Mixture B

10% boron trifluoride etherate in polypropylene glycol of molecular weight 425	0.3 gram

Mixture A was thoroughly stirred and then Mixture B was added. Stirring was continued for a further 10 seconds. After an induction period of 40 seconds the mixture foamed with a rise time of 50 seconds. The foam produced was of fine even texture and air cured to give a smooth light skin. The core density was 1.3 lbs./cu.ft.

EXAMPLE 11.

A prepolymer was prepared as follows: 55 grams (0.5 mole) of resorcinol were dissolved in 246 grams (1.1 mole) of 3,4 - dihydro - 2H pyran - 2 - methyl - (3,4-dihydro - 2H - pyran - 2 - carboxylate) with heating and stirring. This mixture was maintained at 60°C. during the dropwise addition of 2 millilitres of a 20% solution of p-toluenesulphonic acid in ethylene glycol. The temperature of the reaction mixture rose rapidly to 76°C. The reaction mixture was cooled to give a viscous liquid.

The following two mixtures were prepared:

Mixture A

Prepolymer above	25 grams
Siloxane oxyalkylene copolymer type silicone surfactant	0.1 gram
Trichloromonofluoromethane	5 grams

Mixture B

10% boron trifluoride etherate in polypropylene glycol of molecular weight 425	0.4 gram

Mixture A was thoroughly stirred and then Mixture B was added. Stirring was continued for a further 5 seconds. After an induction period of 25 seconds the mixture foamed with a rise time of 29 seconds. The foam produced was white and of even texture with a density of 1.7 lbs./cu.ft.

EXAMPLE 12.

A prepolymer was prepared as follows: 55 grams (0.5 mole) of hydroquinone were dissolved in 246 grams (1.1 moles) of 3,4 - dihydro - 2H - pyran - 2 - methyl-(3,4 - dihydro - 2H -pyran- 2 - carboxylate) with heating and stirring. This mixture was maintained at 60°C. during the dropwise addition 3 millilitres of a 20% solution of p-toluenesulphonic acid in ethylene glycol. The temperature of the reaction mixture rose rapidly to 71°C. The reaction mixture was cooled to give a viscous resin.

The following two mixtures were prepared:

Mixture A

Prepolymer above	16.65 grams
3,4 - dihydro - 2H - pyran - 2 - methyl-(3,4 - dihydro - 2H - pyran - 2 - carboxylate)	8.35 „
Siloxane oxyalkylene copolymer type silicone surfactant	0.1 gram
Trichloromonofluoromethane	5 grams

Mixture B

10% boron trifluoride etherate in polypropylene glycol of molecular weight 425	0.4 gram

Mixture A was thoroughly stirred and then Mixture B was added. Stirring was continued for a further 5 seconds. After an induction period of 95 seconds the mixture foamed with a rise time of 50 seconds. The foam produced was of a light even texture and had a core density of 1.8 lbs. /cu.ft. After an oven cure of 10 seconds at 60°C. the foam had a smooth tough skin.

EXAMPLE 13.

A carbamate was prepared as follows: Methanol (2 moles) was added slowly from a dropping funnel to a stirred mixture of 168 grams of hexamethylene diisocyanate and 0.06 millilitres of N-ethyl morpholine. During the reaction the temperature rose to 150°C. The product solidified at approximately 90°C. A sample recrystallized from benzene had a melting point of 110°C.

A prepolymer was prepared as follows:

The carbamate above	46 grams
3,4 - dihydro - 2H - pyran - 2 - methyl-(3,4 - dihydro - 2H - pyran - 2 - carboxylate)	134 „
Benzene	100 millilitres
p-toluenesulphonic acid	0.3 gram

were heated under reflux for 5 hours. The solvent was then removed by distillation under reduced pressure. The product was a rather viscous liquid, light brown in colour.

The following mixture was prepared:

Prepolymer above	25 grams
Siloxane oxyalkylene copolymer type silicone surfactant	0.1 gram
Trichloromonofluoromethane	5 millilitres
Boron trifluoride etherate in polypropylene glycol of molecular weight 425 (1:1.5 ratio by volume)	1.5 „

The mixture was stirred for 30 seconds and poured into a mould. The mixture was oven cured for 10 minutes at 70°C. and foamed after an induction period of 2 minutes to form a good resilient foam.

EXAMPLE 14.

A polyfunctional amide was prepared as follows: 300 grams of trimerized linseed oil acids were heated under reflux at 190°—210°C. in the presence of a small amount of xylene. A slow current of gaseous ammonia was bubbled into the solution. A total of 17 millilitres of water distilled over in two days. The xylene was then distilled off under reduced pressure. The polyamide product contained 4.48% nitrogen.

A prepolymer was prepared by heating under reflux for 3 hours, 117 grams of the above polyamide product, 115 grams of 3,4 - dihydro - 2H - pyran - 2 - methyl-(3,4 - dihydro - 2H - pyran - 2 - carboxylate), 100 millilitres of benzene and 3 millilitres of ethyl ether saturated with hydrogen chloride. The benzene was then distilled off under reduced pressure. The product was a light brown coloured oil.

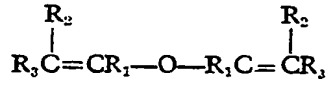
The following mixture was prepared:

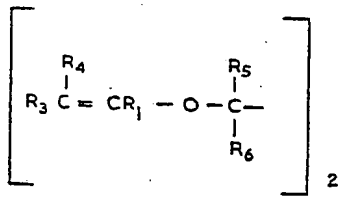
Prepolymer above	12.5 grams
3,4 - dihydro - 2H - pyran - 2 - methyl-(3,4 - dihydro - 2H - pyran - 2 - carboxylate)	12.5 „
Siloxane oxyalkylene copolymer type silicon surfactant	0.1 gram
Trichloromonofluoromethane	5 millilitres
Boron trifluoride etherate in polypropylene glycol of molecular weight 425 (1:1.5 ratio by volume)	3 „

The mixture was stirred for 30 seconds with a mechanical stirrer and poured into a mould. The mixture foamed 44 seconds after the addition of the catalyst and after a rise time of 11 seconds gave a good resilient rigid foam.

WHAT WE CLAIM IS:—

1. A foamable composition comprising (1) at least one prepolymer which is the reaction product of at least one polymerisable ether of the general formula—

I 



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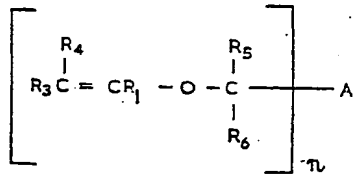
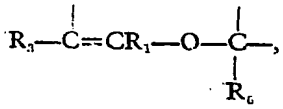


III

wherein n is an integer of minimum value of 2, R_1, R_2 and R_6 are hydrogen or alkyl radicals, R_3 is hydrogen, a halogen atom or a hydrocarbyl radical, R_4 and R_5 taken together are two halogen atoms, two alkyl radicals or an alkylene or substituted alkylene group forming a cyclic structure with the group



and A is a linking group having a valency equal to n, with a compound reactive with the unsaturated linkage of the said polymerisable ether selected from alcohols, polyhydric phenols, carboxylic acids, polycarbamates and polyamides (2) a volatile foaming agent and (3) an acidic catalyst capable of polymerising a vinyl ether.

2. A foamable composition as claimed in Claim 1 including at least one compound selected from polymerisable ethers as hereinbefore defined, phenolic compounds, aliphatic alcohols, epoxidised materials containing at least one epoxide group per molecule, polycarboxylic acids, polyamides, polycarbamates or polymerisable α,β-ethylenically unsaturated compounds.

3. A foamable composition as claimed in Claim 1 or 2 containing from 35% to 98% by weight of the prepolymer.

4. A foamable composition as claimed in any of the preceding claims wherein the prepolymer ingredient is the reaction product of a polymerisable ether as hereinbefore defined and an ether-reactive-group-containing compound in sufficient amount to provide at least one ether-reactive group for each molecule of said polymerisable ether.

5. A foamable composition as claimed in any of the preceding claims wherein the polymerisable ether is 3,4 - dihydro - 2H - pyran - 2 - methyl - (3,4 - dihydro-2H - pyran - 2 -carboxylate).

6. A foamable composition as claimed in any of the preceding claims wherein the prepolymer ingredient is the reaction product of 3,4 - dihydro - 2H - pyran - 2-methyl - (3,4 - dihydro - 2H - pyran - 2 - carboxylate) and a member selected from ethylene glycol, diethylene glycol, 1,5-pentanediol, 2:2-di-p-hydroxyphenyl propane, polypropylene glycol of molecular weight 425, castor oil, glutaric acid chlorendic acid, phloroglucinol, resorcinol, hydroquinone, dimethyl hexamethylenedicarbamate and the amide of trimerised linseed oil acids.

7. A foamable composition as claimed in any of the preceding claims wherein the foaming agent is a halogenated hydrocarbon.

8. A foamable composition as claimed in Claim 7 wherein the foaming agent is trichloromonofluoromethane.

9. A foamable composition as claimed in any of the preceding claims wherein the acid catalyst is boron trifluoride.

10. A foamable composition as claimed in any of the preceding claims wherein the composition includes a surfactant which is a siloxane oxyalkylene copolymer type silicone surfactant.

11. A process for the manufacture of foamed cellular polymeric materials wherein the ingredients of a foamable composition as claimed in any of the preceding claims are mixed and the mixture is allowed to foam.

12. Foamed cellular polymeric materials whenever manufactured from a foamable composition as claimed in any of the preceding claims.

13. A foamable composition according to Claim 1 as hereinbefore described especially with reference to the Examples.

14. A process according to Claim 1 for the manufacture of foamed cellular materials as hereinbefore described especially with reference to the Examples.

15. Foamed cellular polymeric materials whenever manufactured by a process as claimed in Claim 12.

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